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Ab initio work function of elemental metals

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We have used a recently developed self-consistent Green's-function technique based on tight-binding linear-muffin-tin-orbital theory to calculate the work function for the close-packed surfaces of 37 elemental metals. The results agree with the limited experimental data obtained from single crystals to within 15%, and they explain the smooth behavior of the polycrystalline data as a function of atomic number.

The work function is the most fundamental electronic property of a metallic surface, and its determination has been of great importance since the discovery of the photoelectric effect in 1887 by Hertz. The experimental situation up to 1977 is summarized by Michaelson,[1] and a study of his compilation and subsequent measurements reveals that the work functions of the majority of metals are known from measurements on polycrystalline samples only. For the 12 metals where the work function of a particular surface facet has been measured, the polycrystalline and single-surface data differ by as much as 0.5 eV. Furthermore, many of the experimental work functions quoted by Michaelson have not been confirmed by ultrahigh vacuum measurements, and hence there is an uncertainty of unknown magnitude in his recommended values.

In the past two decades there have been several theoretical studies of surface properties starting with the pioneering jellium calculations of Lang and Kohn.[2,3] These model calculations were later improved by Perdew and co-workers,[4-6] and they explained the trends exhibited by the work function of the simple and noble metals. Weinert and Watson[7] used a different approach in the form of overlapping atomic charge densities to estimate the work function of some 30 metals including both simple and transition metals. Their results gave a good description of the experimentally observed trends but overestimated the work functions by, on the average, 80%.

In this situation it is of great importance to be able to calculate work functions *ab initio*. In the past this has been done only in particular cases,[8-24] mainly because of the large computer resources required. Hence, there is no systematic study of surface properties similar to the jellium-model calculations. With the implementation of a self-consistent Green's-function technique[25] based on a recent development of Andersen's tight-binding linear-muffin-tin-orbital (TB-LMTO) method,[26-29] the computational effort needed in surface calculations has been cut by orders of magnitude and a complete *ab initio* study of the work function of all metals is now feasible.

Here, we report a comprehensive series of calculations for the closed-packed surfaces of alkali, alkaline-earth, transition, and noble metals[30] performed by means of the Green's-function TB-LMTO technique described in detail in Skriver and Rosengaard.[25] For exchange correlation we use the functional of Ceperley and Alder,[31] as parametrized by Perdew and Zunger,[32] which we found to give the best overall agreement with the measured work function of the alkali metals. Potentials are treated within the atomic-sphere approximation (ASA) and contain contributions from the first and second, i.e., monopole and dipole, terms in the multipole expansion of the charge density.

Based on convergence tests we use a surface region consisting of three layers of metal plus two layers of empty spheres simulating the vacuum. For the k-space integration we use 45 and 64 special points[33] in the irreducible part of the two-dimensional Brillouin zone for the fcc (111) and bcc (110) surfaces, respectively. Finally, we calculate the moments of the state density by means of a Gaussian integration technique with 12 points distributed exponentially on a semicircle in the complex plane to emphasize the contributions close to the Fermi level. As a result, we expect the calculated work function to be converged to within 0.1 eV.

A measure of the accuracy of the present results would be a comparison with the earlier first-principles surface calculations for the transition metals.[8-24] However, none of these previous calculations have been performed with exactly the combination of surface facet and exchange-correlation potential used in the present work. Since we find that the use of a different exchange-correlation potential alone can change the calculated work function by up to 0.2 eV such a measure of accuracy is not very meaningful. Hence we shall use the less precise criterion of overall agreement with experiment as the figure of merit.

The calculated work functions of the $3d$, $4d$, and $5d$ transition series, which we take to include also the alkali, alkaline-earth, and noble metals, are presented in Fig. 1 together with the experimental values compiled by Michaelson[1] suplemented by recent results for Pt.[34] In the comparison with experiment we note that the calculated work function is in good agreement with the single-crystal data and always above the corresponding polycrystalline data, except for the calcium group. This is to be expected because the most close-packed surface has the highest work function, and hence the theory gives a correct description of the trends exhibited by the experimentally observed work function for the $3d$, $4d$, and $5d$ metals.

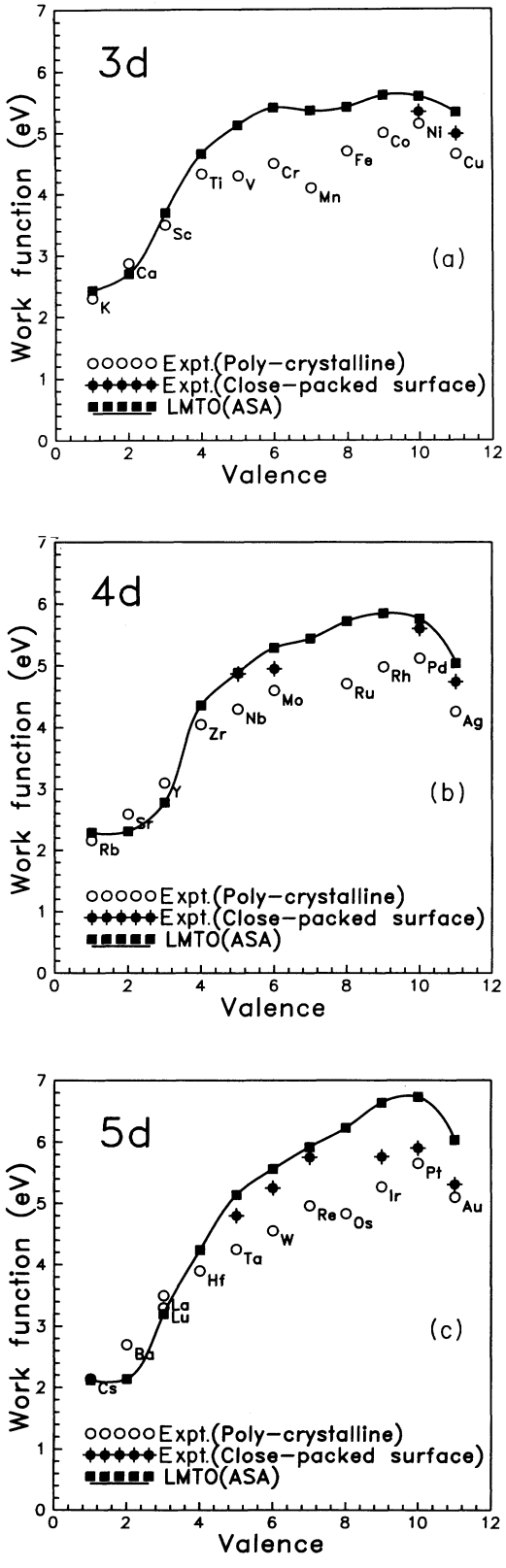

FIG. 1. The calculated work function for the 3*d*, 4*d*, and 5*d* series including the alkali, alkaline-earth, and noble metals compared to available experimental polycystalline data (open circles) and single-surface data (filled circles). The lines connecting the theoretical values are a guide to the eye and valence is defined as the total number of *s*, *p*, and *d* electrons.

Within the ASA, and for one atom per bulk cell, the zero of energy is taken to coincide with the electrostatic potential at the surface of the (neutral) atomic sphere, and the work function W of the corresponding semi-infinite metal may then be expressed as the difference

$$W = \Delta\phi - E_F, \tag{1}$$

between the electrostatic surface dipole $\Delta\phi$ and the Fermi level E_F for the bulk crystal on the ASA energy scale. Since the work functions of the three transition series follow the same trend, when viewed as a function of valence, it will suffice to explain the trend exhibited by the 4*d* series on the basis of the calculated Fermi level and dipole barrier shown in Fig. 2.

Pettifor,[35] Mackintosh and Andersen,[36] and Glötzel[37] found in agreement with our bulk results that the Fermi level in the 4*d* series exhibits a maximum close to Mo. They explained this behavior as the effect of a repulsive ion core whose size, relative to the atomic sphere, attains a maximum in the middle of the series. The *s* electrons respond to being confined in the narrow volume between the core and the atomic sphere by increasing the mean band energy and the bandwidth. Since the number of non-*d* states remains essentially independent of atomic number, the "parabolic" behavior of the Fermi level follows.

In a metal the relative confinement of the *s* electrons results in an increase in the kinetic energy, and for that reason the bulk modulus attains a maximum close to the middle of a transition series. At a surface the *s* electrons will reduce their kinetic energy by spilling out into the vacuum, and therefore the surface dipole also exhibits a "parabolic" dependence on atomic number. As a consequence, the work function obtained as the difference Eq. (1) varies smoothly with atomic number, in agreement with experiment.

Nieminen and Hodges[38] reversed Eq. (1) and deduced

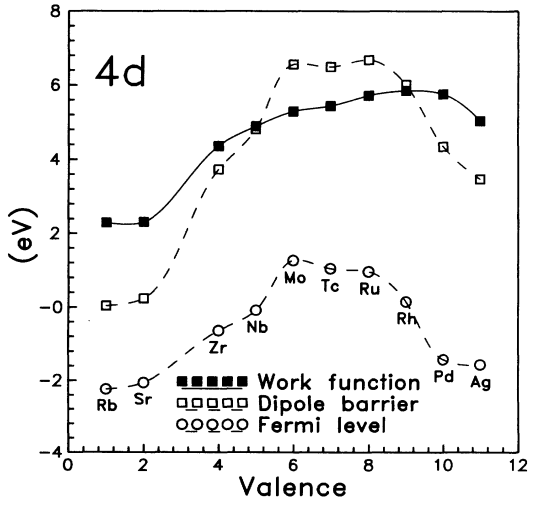

FIG. 2. The calculated work function, dipole barrier, and Fermi level for the 4*d* metals as a function of the total number of *s*, *p*, and *d* electrons.

the surface dipole barrier for transition metals from band estimates of the Fermi level and the experimentally obtained work function. Their results agree with our first-principles values to within 10–30 % which may be considered a surprisingly good agreement in view of the large uncertainties in their procedure. Thus, the present calculations substantiate the notion[38] that the width of the dipole layer varies little with atomic number because it is governed by the screening length, and that the height of the dipole barrier therefore to a large degree is determined by the charge which is able to reduce its kinetic energy by flowing out into the vacuum.

In most of the cases where single-surface data exist, the agreement between theory and experiment is particularly good. This applies to Ni, Cu, Pd, and Ag fcc (111) and to Nb, Mo, Ta, and W bcc (110) where the differences range from 0.0 to 0.4 eV. For Re the difference is 0.2 eV, but here the measurement is performed on the hcp (1011) surface, and hence should not be compared directly with the theoretical fcc (111) value. The largest discrepancies in terms of absolute values are found at the end of the 5*d* series, where the differences for Ir, Pt, and Au fcc (111) range from 0.7 to 0.9 eV, which however is only of the order of 15%. Most probably this discrepancy is partly due to the neglect of higher (than dipole) multipoles in the charge density. This restriction is not fundamental to the method and the higher multipoles will be included in subsequent studies.

In conclusion, we have used a new Green's-function technique in a systematic *ab initio* study of the work function for 37 alkali, alkaline-earth, transition, and noble metals. Our results explain the trends exhibited by the data obtained from measurements on polycrystalline samples and they are in quantitative agreement with the more accurate data obtained on single crystals.

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